Research of oxygen-conducting ceramic materials for lithium chloride melt in reactors for pyrochemical processing of spent nuclear fuel

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Abstract. The behavior of potential ceramic materials (electrolytes conducting on oxygen ions) of electrochemical control devices of technological operations in oxide-halide melts was investigated. Based on the literature data and thermodynamic estimates for long-term tests in the LiCl, LiCl-Li_2O and LiCl-Li_2O-Li melts at a temperature of 650 ° C, mixtures of oxides ZrO_2-Y_2O_3 (YSZ), ZrO_2-Sc_2O_3 (ScSZ), ZrO_2-CaO (CaSZ) and CeO_2-Gd_2O_3 (CGO) were selected. These melt under the studies are the most widely used in a number of high-temperature electrochemical processes of obtaining metals and alloys, as well as in the developed schemes of pyrochemical processing of nuclear fuel. The stability of the samples was determined by changes in mass, appearance, elemental analysis of the melt, as well as via the scanning electron microscopy. The best stability in LiCl-Li_2O melts was shown by the samples of ZrO_2-Y_2O_3 with cubic and tetragonal structures and the samples of ZrO_2-CaO. Based on the changes in the microstructure of the samples, it was concluded that the increase in the content of Li_2O in the LiCl-Li_2O melt accelerates the destruction of the sample mainly by the mechanism of dyeing, and the presence of lithium leads to loosening of the samples.

1. Introduction

Oxide-halide melts are widely used in a number of high-temperature electrochemical processes of obtaining metals and alloys [1-3], as well as in the developed schemes of pyrochemical processing of nuclear fuel [4,5]. The stability and overall efficiency of these processes are largely determined by the ability to control and timely regulation of the process parameters and composition of the studied melts. In particular, it is possible to control the concentration of O^{2-} ions in melts. The potentiometric method using an oxygen electrode is the most common for such measurements [6]. Due to numerous physical and chemical measurements, the regularities of the electrode in the oxide-halide, nitrate, sulphate melts, in solid electrolytes, as well as in liquid metals in the determination of dissolved oxygen are well studied.

Currently, oxygen electrodes or sensors of various types can be used to determine the concentration of O^{2-} ions, as well as the solubility of oxides in chloride melts [7], but most common is oxygen electrode with a ceramic diaphragm $ZrO_2(Y_2O_3)$|Pt, O_2. Regardless of the chosen design of the ion activity sensor O^{2-} it will include a solid electrolyte, as well as metals and/or their oxides as oxygen electrodes. Chemical and thermal stability of materials will largely determine the correctness and duration of the sensor during the technological operations in the studied melts. Most of the materials offered for the manufacture of sensors are not inert in melts based on LiCl chloride containing Li_2O and

other chlorides. However, in the scientific and technical literature there is a lot of work, which studied the laws of oxygen electrodes (mainly Pt|YSZ) and shows the possibility of their use as reference electrodes and indicator electrodes in electrochemical measurements (in particular, in determining the activity of O^{2-} ions) in oxide-chloride melts [8]. In a number of studies on the results of resource tests [9] it was concluded about the stability of materials ZrO_2-Y_2O_3 and ZrO_2-MgO in the melt LiCl-Li_2O without lithium metal.

In this paper, the resource tests of previously unexplored ceramic samples ZrO_2-Sc_2O_3 (ScSZ), ZrO_2-CaO (CaSZ) and CeO_2-Gd_2O_3 (CGO), as well as samples of ZrO_2-Y_2O_3 (YSZ) cubic and tetragonal structure in the melts of LiCl-Li_2O and LiCl-Li_2O-Li were carried out. ScSZ, CaSZ and CGO materials along with YSZ are recommended as solid electrolytes [10], conducted by O^{2-} ions.

2. Experimental part

The experiments were carried out in a cell, the scheme of which is shown in Fig. 1. The glassy carbon (GC) crucible (12) was loaded with the salt LiCl or LiCl pre-prepared by zone recrystallization with the toughened oxide Li2O. The loading was carried out in a closed box in a nitrogen atmosphere. The crucible (12) was placed in a quartz cell (13) protected from LiCl by a nickel screen (14), closed with a fluoroplastic cover (7) with holes for the rod (2) with nickel suspension (gimbal) (9) for samples (10), argon injection (1) and thermocouple (3). Samples (10), compositions and designations of which are presented in Table 2, on the nickel wire (9) fixed on the nickel wire (2) were placed over the salt (11). Then the cell was sealed, vacuumed and gradually heated to operating temperature (650 °C). After that, the purified argon was launched into the cell, and maintained under a small excess pressure throughout the experiment. Further, samples (10) were introduced into the melt and kept in the melt for 150 hours

After the experiment, the samples were lifted from the melt, slowly cooled, removed from the cell and washed in distilled water, dried and the mass measured on the scales of Shimadzu AX200 (ShimadzuCorporation, Japan) with a measurement accuracy of 0.01 mg. The elemental and phase composition of the frozen melt was determined by the inductively coupled plasma spectral emission method and x-ray phase analyses using the spectrometer iCAP 6300 Duo (Thermoscientific, USA), diffractometer Rigaku D/MAX-2200VL/PC (Rigaku, Japan) и Optima 4300 DV (PerkinElmer, USA) with a detection limit of 0,00001-0,001 wt. % and accuracy up to 2 %. The changes in the surface structure of the tetragonal YSZ ceramic sample were additionally investigated by scanning electron microscope JMS-5900LV with microanalysis INCA Energy 200 and INCA Wave 250 (JEOL, UK).

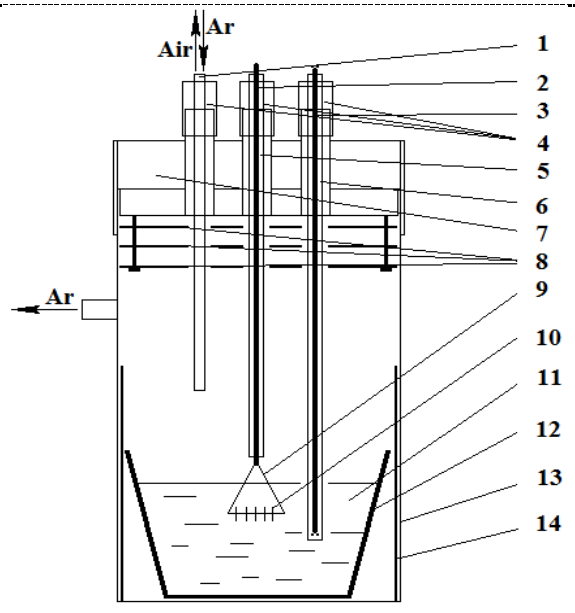


Figure 1. Scheme of the experimental cell for the studies in molten LiCl and LiCl-Li_2O:
1 – Pipe for vacuuming and argon supply;
2 – Nickel rod for suspension; 3 – Thermocouple Pt/Pt-Rh; 4 – Vacuum rubber plugs; 5 – Corundum rod screen; 6 – Corundum case for thermocouple; 7 – Fluoroplastic cover; 8 – Graphite cover screens; 9 – Nickel suspension for samples; 10 – Ceramic samples; 11 – Melt; 12 – Crucible (glassy carbon, MgO); 13 – Quartz cell; 14 – Nickel screen

In experiments with LiCl-Li_2O-Li melts, lithium was introduced into the melt by electrolysis. For this an anode of NiO-Li_2O and a nickel cathode were immersed in the melt through holes in the

fluoroplastic cover. Melt electrolysis was carried out in galvanostatic mode at a cathodic current density of 1.0 A/cm^2. The samples were kept in the melt for 30 hours.

2.1. Resistance of ceramics in LiCL-Li_2O melts

Tests of the sample YSZ (tetragonal) in the melt of LiCl, which does not contain Li_2O in the atmosphere of argon for 150 hours showed that the interaction of ceramics with the melt does not occur. After washing in distilled water, it was visually found that the shape and color of the sample YSZ saved. The mass of the sample has not changed. According to chemical analysis, the content of zirconium and yttrium in the frozen salt melt after the experiment was not more than 0,0010 and 0,0004 wt. %, respectively.

As shown in Fig. 2, during the exposure of five ceramic samples in LiCl melts with 1.5 and 5 wt. % Li2O oxide samples also retained color and shape, except for the ScSZ sample, which collapsed in both experiments. Ceramic CGO samples after exposure in LiCl melts with 1.5 and5 wt. % Li_2O oxide within 150 h changed its color from light gray to dark gray. According to the literature data [11,12] this is due to the fact that in conditions of low concentrations of oxygen there is a change in the valence of cerium in the oxide from IV to III, i.e. the oxide molecule loses one atom of oxygen. Despite the improvement of electrochemical characteristics (increase in total conductivity), the function of this ceramics in the oxygen electrode can be broken, because it appears electronic conductivity.

Figure 2. I Washed ceramic samples after exposure in the melt LiCl with 1.5 wt. % Li_2O for 150 h at 650 °C

2.2. Resistance of ceramics in LiCL-Li_2O-Li

For further corrosion tests in the melt LiCl with 1.5 wt. % Li_2O, lithium metal was selected three sample: YSZ(tetragonal), YSZ (cubic) and CaSZ, which, according to the results of previous tests, were the most acceptable in terms of chemical and thermal stability.

Figure 3 shows photos of samples after aging in the melt LiCl with 1.5 wt. % Li_2O in the presence of lithium for 30 h at 650 °C. It can be seen that the samples have not undergone significant geometric and weight changes. However, the color of the samples became partially dark gray, which indicates the restoration of oxide ceramic samples with metallic lithium. Since the composition of ceramics changes under the influence of lithium metal, the electrochemical characteristics of the sample (conductivity by O^{2-} ions, electronic conductivity) can also change significantly. In this regard, the properties of the samples both separately and in the oxygen electrode after exposure to lithium require a separate study.

Figure 3. Washed ceramic samples after exposure in the melt LiCl with 1.5 wt. % Li_2O in the presence of lithium for 30 h at 650 °C

2.3. The structure of the samples after exposure in melts LiCl-Li_2O and LiCl-Li_2O-Li

For studies of structural changes using scanning electron microscopy samples were selected YSZ (tetragonal) and CaSZ, as among other materials have optimal performance. In particular the mechanical strength of YSZ (tetragonal) is higher than YSZ(cubic).

Table 1. Electron micrographs of the samples YSZ and CaSZ after exposure in the molten LiCl-Li_2O and LiCl-Li_2O-Li

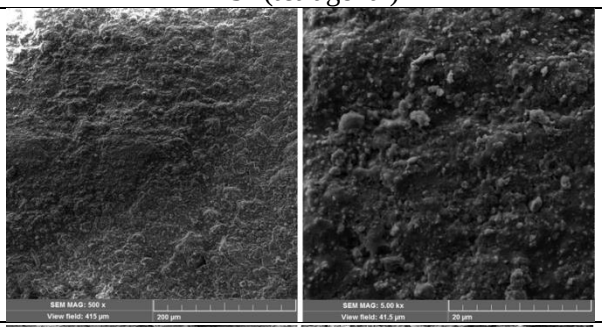
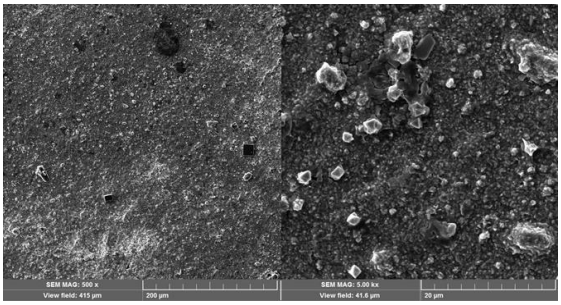
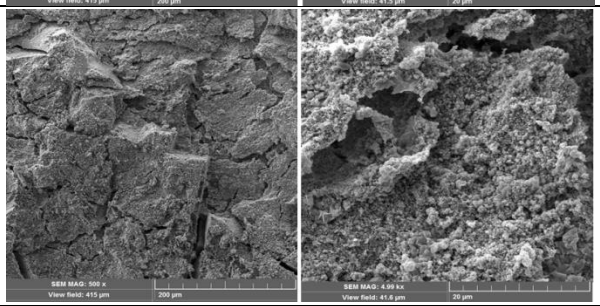
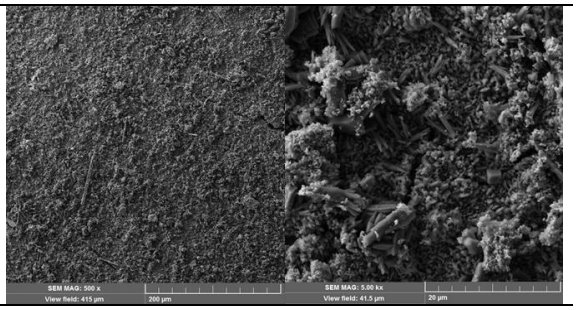
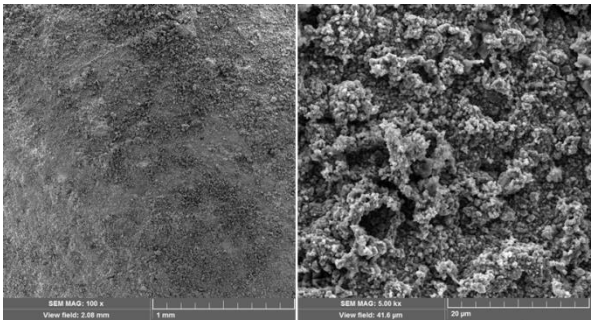
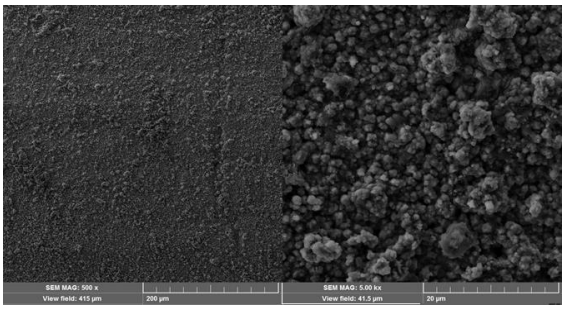
	YSZ(tetragonal)	CaSZ
150 h in the melt LiCl-1.5 wt.% Li_2O		
150 h in the melt LiCl-5 wt.% Li_2O		
30 h in the melt LiCl-1.5 wt.% Li_2O-Li		

Table 1 presents microphotographs of samples before and after exposure in LiCl melts with 1.5 and 5 wt. % Li_2O oxide for 150 h, and after holding in the melt LiCl with 1.5 wt. % Li_2O oxide in the presence of lithium for 30 h at 650 °C.

For both samples, a relative preservation of the surface density is observed except that the surface of the sample is YSZ (tetragonal) became more developed, and on the surface of CaSZ appeared inclusions of yttrium, cerium and gadolinium oxides (according to SEM-EDX). After exposure in the melt LiCl with 5 wt. % Li_2O for 150 h and in the melt LiCl with 1.5 wt. % Li_2O becomes loose and porous in the presence of lithium for 30 h on the sample surface. On the sample YSZ (tetragonal) after holding in the melt LiCl with 5 wt. % Li_2O for 150 h was visible detachment. The destruction of the sample under these conditions occurs mainly by the mechanism of dyeing (the introduction of Li_2O into the YSZ grid, the occurrence of tension and detachment).

In general, microstructural studies indicate that ceramic materials are based on YSZ (tetragonal) and CaSZ can be recommended for use in LiCl-Li_2O melts as oxygen-conducting diaphragms of electrochemical devices. However, with an increase Li_2O and with the appearance of lithium metal in the melts, their duration will be reduced and determined by the thickness of the diaphragms and the ability of the latter to maintain the type of conductivity. The results of the behavior of YSZ ceramics obtained above are consistent with the results of [13].

3. Conclusion

The behavior of materials ZrO_2-Y_2O_3 (YSZ), ZrO_2-Sc_2O_3 (ScSZ), ZrO_2-CaO (CaSZ) и CeO_2-Gd_2O_3 (CGO) at their long exposure in LiCl-Li_2O melts with concentration of lithium oxide 1.5 and 5 wt % was studied, as well as in the melt LiCl-Li2O in the presence of lithium metal at a temperature of 650 °C.

The thermodynamic evaluation of the chemical stability of the materials of the samples with the components of the melt LiCl-Li_2O and lithium was carried out. It is shown that in LiCl-Li_2O melts the samples should be sufficiently stable due to the slowness of heterophase reactions of ceramic oxides with lithium oxide. In the presence of lithium in the melt, the most stable oxides are CaO, CeO_2 and Gd_2O_3, so the resistance of ceramics in such melts will be determined mainly by the interaction of lithium with ZrO_2.

Based on the results of resource tests in the LiCl- Li_2O melts, it was shown that the sample of ZrO_2 doped with Sc_2O_3 oxide is thermally unstable, and the sample from the mixture of CeO_2 and Gd_2O_3 oxides is chemically unstable. The best resistance in the melt LiCl- Li_2O samples have ZrO_2-Y_2O_3 and ZrO_2-CaO. At the same time, according to microstructural studies in the melt LiCl-Li2O with a concentration of lithium oxide 5 wt.%, as well as in the melt LiCl- Li_2O in the presence of lithium metal, these samples are less stable. Consequently, the increase in the content of Li_2O and the emergence of the lithium in the melt contribute to the destruction of the sample and can reduce the duration of operation of the sensor ions O^{2-} in conditions of direct contact of the ceramics with the investigated melt. This should be taken into account when determining the operating time of the sensors in technological process.

4. References

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